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SYNTHESIS AND PROPERTIES OF DICYCLOPENTADIENYLTANTALUM HYDRIDE OLEFIN COMPOUNDS

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Summary

Reactions of Cp_2TaCl_2 with RMgCl (R = n-C_3H_7, i-C_3H_7, n-C_4H_9, s-C_4H_9, n-C_5H_{11} and C_5H_9) give tantalum hydride π-olefin complexes $Cp_2Ta(H)L$ (L = C_3H_6, C_4H_8, C_5H_{10} and C_5H_8). Two isomers of $Cp_2Ta(H)C_3H_6$ were obtained. The complexes are useful starting materials for the synthesis of other tantalum hydride species, e.g. $Cp_2Ta(H)PEt_3$ and Cp_2TaH_3.

Introduction

Transition metal hydride olefin complexes are postulated as intermediates in hydrozirconation, the reaction of $Cp_2Zr(H)Cl$ with olefins [1], and in the reaction of olefins with the system Cp_2TiCl_2/i-PrMgBr [2]. These unstable complexes probably decompose via a rapid insertion of the coordinated olefin into the metal—hydride bond. Only very few stable compounds with an olefin *cis* to a hydride ligand are known [3,4]. In 1971 Tebbe and Parshall reported the preparation of a niobium hydride ethylene complex from Cp_2NbH_3 and C_2H_4. They suggested the existence of a similar tantalum compound but gave no details of its preparation or characterization. In this paper we report a convenient method for the preparation of some new tantalum and niobium hydride olefin complexes $Cp_2M(H)L$, and discuss the metal—olefin bond in the tantalum hydride—propylene complex.

Results and discussion

Reaction of Cp_2TaCl_2 with 2 mol of RMgCl (R = n-C_3H_7, i-C_3H_7, n-C_4H_9, s-C_4H_9, n-C_5H_{11} and C_5H_9) in ether and subsequent extraction with pentane gives microcrystalline yellow or red products $Cp_2Ta(H)L$ (L = C_3H_6, C_4H_8, C_5H_{10} and C_5H_8) in moderate yields (Table 1). The products are air-sensitive and soluble in common, non-halogenated organic solvents. Elemental analyses

TABLE 1

ANALYTICAL DATA FOR THE COMPOUNDS $Cp_2Ta(H)L$

Compound	Grignard reagent [a]	Yield (%)	Colour	Analysis (found (calc.) (%))		
				C	H	Ta
$Cp_2Ta(H)CH_2{=}CHCH_3$ (a) [b]	n-C_3H_7MgCl	60	Yellow	44.40 (44.08)	5.01 (4.84)	50.89 (51.08)
$Cp_2Ta(H)CH_2{=}CHCH_2CH_3$ (a)	n-C_4H_9MgCl	55	red	45.73 (45.66)	5.33 (5.20)	49.15 (49.14)
$Cp_2Ta(H)CH_2{=}CHCH_2CH_3$ (b)	s-C_4H_9MgCl	15	purple	45.10 (45.66)	5.34 (5.20)	48.78 (49.14)
$Cp_2Ta(H)CH_2{=}CHCH_2CH_2CH_3$	n-$C_5H_{11}MgCl$	30	red	46.90 (47.13)	5.51 (5.54)	47.37 (47.33)
$Cp_2Ta(H)\underline{CH_2CH{=}CHCH_2}CH_2$	C_5H_9MgCl	55	yellow	47.19 (47.38)	5.09 (5.04)	47.50 (47.59)

[a] Here the reagent used in the preparation is given. [b] (a) and (b) are used for distinguishing the isomers.

TABLE 2

PMR DATA FOR THE $Cp_2Ta(H)L$ COMPOUNDS [a,b]

Compound	H_{Cp}	H	H_L
$Cp_2Ta(H)CH_2{=}CHCH_3$ (a)	4.49 s, 4.36 s	—3.10 s	2.2—0.1 m
$Cp_2Ta(H)CH_2{=}CHCH_3$ (b)	4.40 s, 4.36 s	—3.36 s	1.8—0.1 m
$Cp_2Ta(H)CH_2{=}CHCH_2CH_3$ (a)	4.44 s, 4.34 s	—3.05 s	2.2—0.1 m
$Cp_2Ta(H)CH_2{=}CHCH_2CH_3$ (b)	4.43 s, 4.39 s	—3.68 s	1.9—0.1 m
$Cp_2Ta(H)CH_2{=}CHCH_2CH_2CH_3$ (a)	4.51 s, 4.38 s	—3.32 s	2.3—0.1 m
$Cp_2Ta(H)ÇH_2CH{=}CHCH_2ÇH_2$	4.36 s	—3.03 s	3.5—0.6 m

[a] C_6D_6 solution, 35° C, TMS as an internal standard. [b] Values are given in δ (ppm); s singlet; m multiplet.

(Table 1), chemical and physical properties are in agreement with the formula $Cp_2Ta(H)L$.

The hydride olefin complexes are monomeric (by cryoscopy in benzene) and diamagnetic.

The IR spectra are all very similar, showing the characteristic frequencies of π-bonded cyclopentadienyl groups in the usual ranges. The C=C stretching frequencies of the olefin ligands are found at about 1450 cm^{-1}, and indicate considerable weakening of the π-bond of the olefin as a result of the coordination to tantalum. Bands in the 1750—1800 cm^{-1} range are assigned to ν(Ta—H).

The mass spectra of the hydride-olefin complexes show a strong peak at m/e 312 (Cp_2TaH^+) and metastable peaks corresponding to $Cp_2Ta(H)L^+ \rightarrow Cp_2TaH^+ + L$, illustrating the stability of the Ta—H bond and the easy loss of the olefin.

The PMR spectra of the complexes $Cp_2Ta(H)L$ (Table 2) show two resonances due to the two non-equivalent π-bonded cyclopentadienyl rings (for $L = C_5H_8$ (cyclopentene) they coincide) and a single absorption at high field of the hydride H. In most cases the olefin resonances are very complicated and only for $Cp_2Ta(H)C_3H_6$ a detailed interpretation is possible. A computer simulation of the $ABCD_3$ spin system of the propene group exactly fits the PMR spectrum observed for $Cp_2Ta(H)C_3H_6$ (Fig. 1).

If the Ta(C=C)H system is approximately planar then *endo*- and *exo*-isomers of the complex are possible (Fig. 1) [4]. Reaction of Cp_2TaCl_2 with i-PrMgCl indeed yields two isomers (ratio about 1/1), whereas the reaction with n-PrMgCl gives one isomer. For the olefin complexes prepared from the higher alkyls more isomers are possible, depending on the position of the double bond in the chain. For instance, for L = 1-butene, two isomers (*endo*- and *exo*-ethyl) are possible, and for 2-butene *cis*- and *trans*-olefin complexes are expected. The experiments show that from n-BuMgCl only one isomer of the 1-butene complex (*endo* or *exo*) is formed, a result very similar to that in the reaction with n-PrMgCl. With s-BuMgCl both 1-butene and 2-butene complexes are conceivable. The PMR spectrum clearly shows that the product is exclusively a 1-butene complex, but it is not the same isomer as that obtained from n-BuMgCl. An unequivocal identification of the isomers on the basis of PMR spectroscopy is not possible. Provisionally, we use (a) and (b) for the series of related isomers of $L = C_3H_6$, C_4H_8 and C_5H_{10} . The structural analogy is inferred

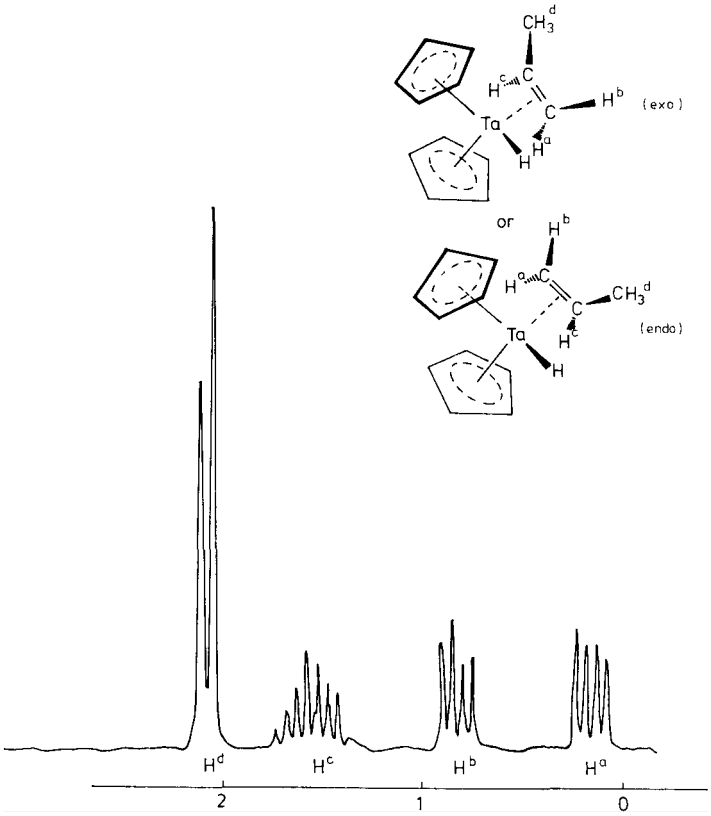


Fig. 1. PMR spectrum of $Cp_2Ta(H)C_3H_6$ (a) (alkyl region). $Cp_2Ta(H)C_3H_6$ (a): H^a 0.14, H^b 0.83, H^c 1.58, H^d 2.13 ppm. J_{ab} 5, J_{ac} 10.5, J_{ad} 0.5, J_{bc} 10.5, J_{bd} 0.5, J_{cd} 6 Hz. $Cp_2Ta(H)C_3H_6$ (b): H^a 0.14, H^b 0.83, H^c 1.58, H^d 1.81 ppm. J_{ab} 5, J_{ac} 10.5, J_{ad} 0.5, J_{bc} 10.5, J_{bd} 0.5, J_{cd} 6 Hz.

from the positions of the various group resonances in the PMR spectra (Table 2). The relatively low-field resonance of the methyl hydrogen atoms observed for isomer (a) of $Cp_2Ta(H)C_3H_6$ may be assigned to the *endo*-isomer since deshielding of the methyl hydrogen of the *endo*-isomer by both a Cp-group and the hydride hydrogen may be expected; however this reasoning is somewhat speculative. Benfield and Green [4] have studied and assigned *endo*- and *exo*-isomers of $[Cp_2W(H)C_3H_6]^+$, but no data which would be helpful for our problem were given. The different chemical environment of the Cp-groups, that leads to a splitting of the Cp signal, is easily explained by the coordination of the olefin (Fig. 1).

The mechanism of the formation of the hydride-olefin complexes is not yet known, but it seems reasonable to suppose a crucial role for β-hydrogen in the last step of the reaction e.g. β-H abstraction (Scheme 1). In that case a preferen-

SCHEME 1

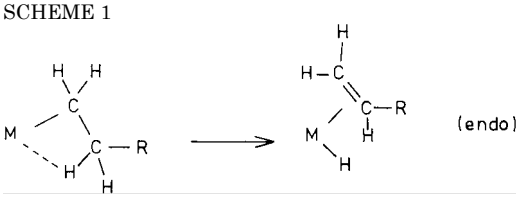


TABLE 3

^{13}C NMR data [a]

$Cp_2Ta(H)C_3H_6$ (a)	$Cp_2Nb(H)C_2H_4$	$Cp_2Nb(C_2H_5)C_2H_4$
δ(C(Cp')) 91.13 ppm	δ(C(Cp)) 91.11 ppm	δ(C(Cp)) 97.57 ppm
δ(C(Cp")) 90.91 ppm		
(178 Hz) [b]	(176 Hz)	(174 Hz)
δ(C(CH_2)) 15.11 ppm	δ(C(CH_2)) 13.44 ppm	δ(C(CH_2)) 29.35 ppm
(144 Hz)	(153 Hz)	(153.5 Hz)
δ(C(CH)) 16.16 ppm	δ(CH_2) 7.96 ppm	δ(C(CH_2)) 27.63 ppm
(148 Hz)	(156 Hz)	(154.5 Hz)
δ(C(CH_3)) 28.23 ppm		δ(C(CH_2)) 11.18 ppm
(126 Hz)		(122 Hz)
		δ(C(CH_3)) 20.25 ppm
		(130.5 Hz)

[a] C_6D_6 solution, 35° C, TMS as an internal standard. [b] ^{13}C—^{1}H coupling constants in parentheses.

tial formation of one isomer of the complex is understandable. The observation that no hydride-olefin complexes are formed from alkyl groups without β-H (when e.g. R = CH_3, $CH_2C_6H_5$ and $CH_2C(CH_3)_3$, Cp_2TaR_2 is formed instead [5]), supports our view.

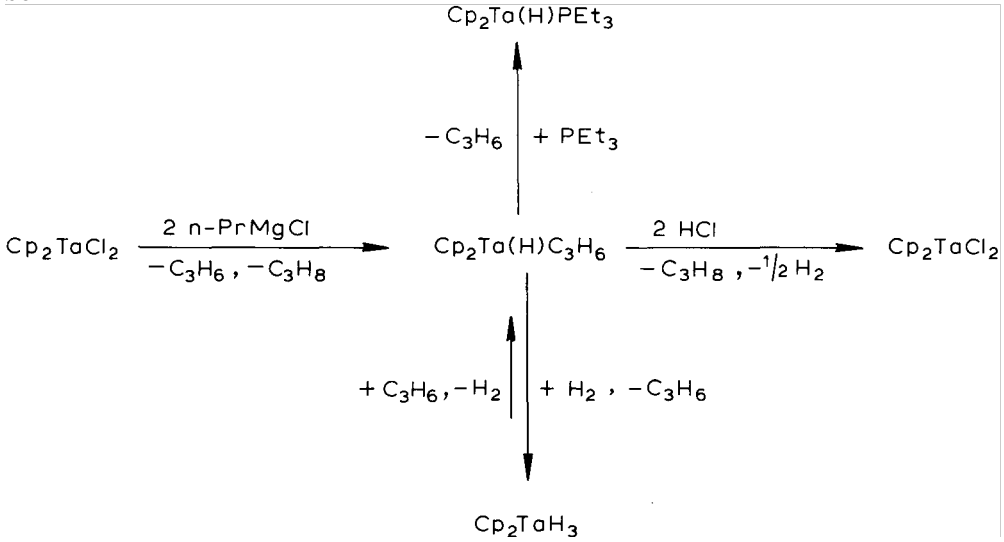
The large change in chemical shift of the olefinic carbons in the ^{13}C NMR spectra of the niobium compounds $Cp_2Nb(H)C_2H_4$ and $Cp_2Nb(C_2H_5)C_2H_4$ [6] is also observed for $Cp_2Ta(H)C_3H_6$ (a) (Table 3), indicating a metal(d)-to-olefin (π^*) back-donation and consequently a weakening of the C—C π bond. This is consistent with the low frequency ν(C=C), observed in the IR spectra.

The ^{13}C—^{1}H coupling constants of the tantalum complex compared with those of the simple alkanes (J 125 Hz) and ethylene (J 156.4 Hz) indicate that partial rehybridization of the olefinic carbons to sp^3 has taken place. A similar effect has been observed in the molecular structure of $Cp_2Nb(C_2H_5)C_2H_4$, where the olefin is non-planar and the hydrogen atoms bend away from the metal [6]. The reaction of $Cp_2Ta(H)C_3H_6$ with H_2 (1 atm) affords Cp_2TaH_3 in good yield. This procedure is a good alternative for the conventional synthesis of Cp_2TaH_3, which is poorly reproducible [7]. The reverse reaction of Cp_2TaH_3 with propene again yields $Cp_2Ta(H)C_3H_6$; no further reaction, e.g. insertion or polymerization, occurs, probably because of steric effects and the lower reactivity of tantalum hydride compounds compared with the corresponding niobium species. In this way the *endo*- and *exo*-methyl isomers of $Cp_2Ta(H)C_3H_6$ are obtained in a ratio of about 1/1, while the Grignard method yields essentially one isomer.

Reaction of $Cp_2Ta(H)C_3H_6$ with an excess of PEt_3 in toluene gives red, crystalline $Cp_2Ta(H)PEt_3$, which was also obtained from the reaction of Cp_2TaH_3 and PEt_3 [8]. Reaction of $Cp_2Ta(H)C_3H_6$ with HCl in ether yields propane, dihydrogen and Cp_2TaCl_2. The reactions mentioned above are summarized in Scheme 2.

The compounds $Cp_2Ta(H)L$ are thermally rather stable: $Cp_2Ta(H)C_3H_6$ (a) can be sublimed at 95°C/0.05 mmHg. Above this temperature partial conversion into isomer (b) is observed and decomposition of the hydride olefin com-

SCHEME 2



plex starts. A detailed study of the thermal behaviour of the complexes will be reported elsewhere. Because of the supposed close relationship of the dicyclopentadienyl compounds of Nb and Ta we expected that reactions of Cp_2NbCl_2 with RMgCl (R = n-C_3H_7, i-C_3H_7, n-C_4H_9, s-C_4H_9, n-C_5H_{11} and C_5H_9) would lead to the compounds $Cp_2Nb(H)L$. However, so far only the reactions with n-PrMgCl, i-PrMgCl, and n-BuMgCl gave hydride olefin complexes. These reactions are still under investigation.

Experimental

All experiments were carried out under purified nitrogen. Solvents were distilled from $LiAlH_4$ or dried over Na wire (toluene). Cp_2TaCl_2 and Cp_2TaH_3 were prepared by published procedures [9,7]. IR spectra were measured on a Hitachi EPI-G spectrophotometer using a Nujol mull between KBr plates. The mass spectra were recorded on an AEI-MS9 instrument by Mr. A. Kiewiet, ^{13}C NMR and PMR spectra were recorded on a Varian XL-100 instrument. The computer simulation was performed by Drs. W.A. Mellink with the program SIMEQ-16 on the 620 F computer of the XL-100. Elemental analyses were performed at the Microanalytical Department of this University under supervision of Mr. A.F. Hamminga.

Preparation of $Cp_2Ta(H)C_3H_6$ (a)

To a stirred suspension of Cp_2TaCl_2 (760 mg, 2 mmol) in 40 ml of ether 4.1 ml of n-C_3H_7MgCl in ether (0.98 *M*) was slowly added at room temperature. After the colour of the suspension had gradually changed from brown to yellow (5—6 h), the solvent was removed under reduced pressure and the residue extracted with n-pentane. The pentane solution was concentrated and cooled to —78°C. Yellow crystals separated. Yield: 420 mg $Cp_2Ta(H)C_3H_6$(a) (60%). The other complexes $Cp_2Ta(H)L$ were prepared in essentially the same way (Table 1).

Reaction of $Cp_2Ta(H)C_3H_6$ with H_2

A solution of $Cp_2Ta(H)C_3H_6$ (280 mg, 0.8 mmol) in 10 ml of toluene was stirred for 14 h at 90°C under hydrogen (1 atm). The yellow-green solution was filtered and the solvent removed under reduced pressure. After washing with pentane a pale-yellow product was isolated. Yield: 160 mg Cp_2TaH_3, (65%, IR, PMR).

Reaction of Cp_2TaH_3 with propene

A solution of Cp_2TaH_3 (340 mg, 1.1 mmol) in 10 ml of toluene was stirred for 12 h at 90°C under propene. After evaporation the brown residue was extracted with n-pentane. The pentane solution was concentrated and cooled to —78°C. Light-reddish material was separated and was isolated. Yield: 40 mg $Cp_2Ta(H)C_3H_6$ (10%), which was a 1/1 mixture of the *endo*- and *exo*-methyl isomers (PMR).

Reaction of $Cp_2Ta(H)C_3H_6$ with PEt_3

To a solution of $Cp_2Ta(H)C_3H_6$ (315 mg, 0.9 mmol) in 10 ml of toluene 0.5 ml of PEt_3 (~4 mmol) was added. The mixture was stirred for 12 h at 90°C, the solvent was removed in vacuo, and the residue extracted with n-pentane. The extract was concentrated and slowly cooled to —78°C. Red crystals separated and were washed with cold pentane and isolated. Yield: 80 mg $Cp_2Ta(H)PEt_3$ (18%, IR, PMR).

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